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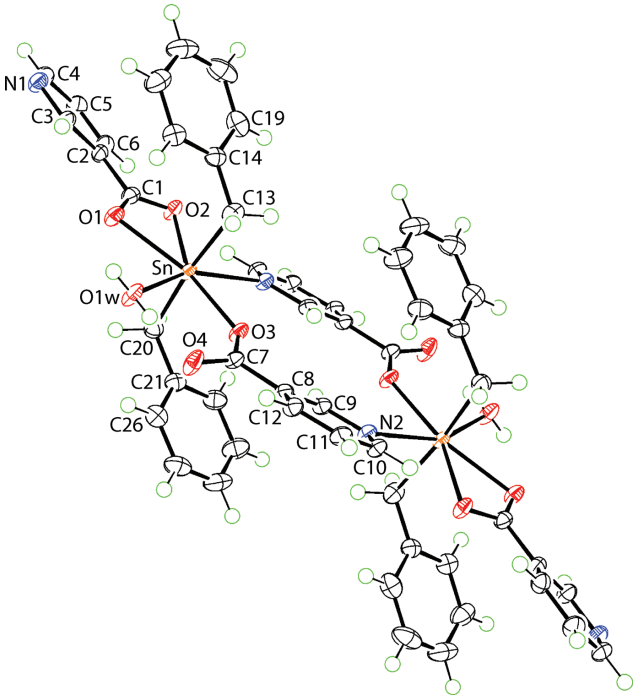
Crystal structure of di-μ-nicotinato-κ²*N*:*O*; κ²*O*:*N*-bis-[aqua-bis(benzyl)(nicotinato-κ²*O*,*O*′)tin(IV)], $C_{52}H_{48}N_4O_{10}Sn_2$



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Abstract

$C_{52}H_{48}N_4O_{10}Sn_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.4845(1)$ Å, $b = 9.2814(1)$ Å, $c = 15.5517(2)$ Å, $\alpha = 83.005(1)°$, $\beta = 81.918(1)°$, $\gamma = 74.690(1)°$, $V = 1164.87(2)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0173$, $wR_{ref}(F^2) = 0.0453$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.11 × 0.08 × 0.07 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	9.07 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	27999, 4156, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4058
$N(param)_{refined}$:	313
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.66898(2)	0.50068(2)	0.25614(2)	0.01211(5)
O1	0.77407(15)	0.51536(14)	0.10986(8)	0.0165(3)
O2	0.57406(15)	0.70805(14)	0.14928(8)	0.0168(3)
O3	0.67098(15)	0.39034(13)	0.39351(8)	0.0145(3)
O4	0.85574(16)	0.16602(15)	0.39145(8)	0.0209(3)
O1W	0.84655(16)	0.28408(15)	0.23436(8)	0.0192(3)
H1W	0.861(3)	0.237(2)	0.2838(9)	0.029*
H2W	0.9337(19)	0.279(3)	0.2002(13)	0.029*
N1	0.86193(19)	0.75449(17)	−0.13240(10)	0.0178(3)
N2	0.56121(18)	0.31654(16)	0.66122(10)	0.0138(3)
C1	0.6800(2)	0.6428(2)	0.09213(12)	0.0141(4)
C2	0.6949(2)	0.71874(19)	0.00210(11)	0.0138(4)
C3	0.8423(2)	0.6875(2)	−0.05167(12)	0.0165(4)
H3	0.933567	0.615357	−0.030338	0.020*
C4	0.7313(2)	0.8554(2)	−0.16177(12)	0.0185(4)
H4	0.743511	0.902209	−0.219276	0.022*
C5	0.5801(2)	0.8945(2)	−0.11258(12)	0.0187(4)
H5	0.491006	0.967146	−0.135560	0.022*
C6	0.5613(2)	0.8254(2)	−0.02904(12)	0.0167(4)
H6	0.458985	0.850235	0.006492	0.020*
C7	0.7549(2)	0.2685(2)	0.42943(12)	0.0137(4)
C8	0.7297(2)	0.25006(19)	0.52733(11)	0.0132(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C9	0.5862(2)	0.32714(19)	0.57387(11)	0.0130(3)
H9	0.502051	0.390246	0.542269	0.016*
C10	0.6823(2)	0.2264(2)	0.70494(12)	0.0148(4)
H10	0.666590	0.218358	0.766866	0.018*
C11	0.8284(2)	0.1450(2)	0.66368(12)	0.0155(4)
H11	0.910499	0.082157	0.696758	0.019*
C12	0.8528(2)	0.1566(2)	0.57362(12)	0.0144(4)
H12	0.951898	0.101845	0.543762	0.017*
C13	0.8391(2)	0.6103(2)	0.29358(12)	0.0186(4)
H13A	0.780924	0.676176	0.339722	0.022*
H13B	0.928179	0.532738	0.319560	0.022*
C14	0.9160(2)	0.7023(2)	0.22279(12)	0.0163(4)
C15	1.0568(2)	0.6360(2)	0.16963(13)	0.0193(4)
H15	1.102673	0.530923	0.178094	0.023*
C16	1.1312(3)	0.7207(2)	0.10463(13)	0.0254(4)
H16	1.227010	0.673473	0.069096	0.030*
C17	1.0658(3)	0.8739(3)	0.09160(14)	0.0297(5)
H17	1.117361	0.932418	0.047747	0.036*
C18	0.9248(3)	0.9415(2)	0.14283(15)	0.0299(5)
H18	0.878712	1.046456	0.133589	0.036*
C19	0.8503(2)	0.8563(2)	0.20776(14)	0.0230(4)
H19	0.753303	0.903757	0.242356	0.028*
C20	0.4728(2)	0.4124(2)	0.22963(12)	0.0162(4)
H20A	0.383163	0.496442	0.209408	0.019*
H20B	0.513763	0.346086	0.181724	0.019*
C21	0.4043(2)	0.3259(2)	0.30670(12)	0.0165(4)
C22	0.2649(2)	0.3926(2)	0.36056(13)	0.0205(4)
H22	0.209861	0.494523	0.347231	0.025*
C23	0.2054(2)	0.3122(2)	0.43332(14)	0.0259(4)
H23	0.110367	0.359352	0.469403	0.031*
C24	0.2843(3)	0.1628(2)	0.45358(14)	0.0267(5)
H24	0.244144	0.107730	0.503568	0.032*
C25	0.4217(3)	0.0953(2)	0.40035(14)	0.0240(4)
H25	0.475735	−0.006976	0.413618	0.029*
C26	0.4813(2)	0.1754(2)	0.32778(13)	0.0203(4)
H26	0.576016	0.127353	0.291795	0.024*

Source of material

Dibenzyltin dichloride was synthesized by the direct reaction of benzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Dibenzyltin oxide was prepared from the 1:1 molar reaction of dibenzyltin dichloride with sodium hydroxide. Dibenzyltin oxide (0.64 g, 2.0 mmol) and nicotinic acid (Sigma-Aldrich; 0.48 g, 4.0 mmol) were heated in 95% ethanol (50 mL) and stirred for 3 h. After filtration, the filtrate was evaporated slowly until colourless crystals were formed.

Yield: 0.15 g (47%). **M.pt** (Mel-temp II digital melting point apparatus): 459–461 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1598 (s) ν(C=O), 1471 (m) ν(C—C), 1029 (m) ν(C—O), 694 (m) ν(Sn—N), 581 (m) ν(Sn—O). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer, chemical shifts relative to Me_4Si, $CDCl_3$ solution at 50 °C; ppm): 2.20 (s, 4H, CH_2), 4.58 (b, 2H, OH_2), 7.27–7.94 (m, 10H, Ph—H), 8.05–8.78 (m, 8H, Ph—H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 32.3 (CH_2), 119.9, 120.3, 120.6, 122.2, 123.1, 123.5, 123.7, 123.9, 124.1, 124.4, 132.1, 133.6, 146.3, 148.0 (Ph—C), 166.0 (CO), 169.2 (CO).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H atoms were refined with O—H = 0.84 ± 0.01 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Comment

It is well-established that organotin carboxylates adopt a very wide range of structural motifs in their crystals [6], often depending in an capricious fashion, upon the remote substituents bound to the carboxylate ligands. Molecules of the general formula $R_2Sn(O_2CR')_2(OH_2)$ are based on a pentagonal-bipyramidal geometry with the chelating carboxylate ligands and water molecule contributing O atoms to the pentagonal plane, and the tin-bound organic substituents occupying axial positions. This is the common motif as found in $(c\text{-}C_6H_{11})_2Sn(O_2CMe)_2(OH_2)$ [7] and several other examples reported over the years [8–13]. While it is normal for new structural motifs to occur when potential N-donor atoms are incorporated in the carboxylate ligand [6], this was not the case for $(4\text{-}ClC_6H_4CH_2)_2Sn(O_2CC_5H_4N\text{-}3)_2(OH_2)$ [14], which was found to adopt the common structural motif. However, when the chloro substituent in the benzyl group is replaced by a bromo substituent, a new, binuclear motif is found whereby the pyridyl-N of one carboxylate ligand, now coordinating via one O atom only, bridges a centrosymmetrically-related Sn atom [15], again leading to a pentagonal-bipyramidal geometry, albeit one based on a trans-C_2NO_4 donor set. In this context and in continuation of recent studies of pyridyl-substituted carboxylates [16], the crystal and molecular structures of the "parent" $(C_6H_5CH_2)_2Sn(O_2CC_5H_4N\text{-}3)_2(OH_2)$, (I), is described herein.

The molecular structure of binuclear (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation $1 - x$, $1 - y$, $1 - z$). The binuclear molecule in (I) is disposed about a centre of inversion, and two distinct modes of coordination of the carboxylate ligands are evident. The O1-carboxylate ligand chelates a Sn atom, forming Sn—O bond lengths [Sn—O1 2.3253(12) Å & Sn—O2 2.4276(12) Å] that differ by about 0.1 Å. The O3-carboxylate ligand is bridging, coordinating the Sn atom via one O atom [Sn—O3 = 2.2542(12) Å & Sn···O4 = 3.6515(13) Å] and the

centrosymmetrically-related Sn atom via the 3-pyridyl-N2 atom [Sn—N2 = 2.5337(15) Å]. The NO_4, approximate pentagonal plane, is completed by the water-O1w atom [Sn—O1w = 2.2021(13) Å] and the axially-coordinated methylene-C atoms [Sn—C13 = 2.1484(18) Å & Sn—C20 = 2.1470(18) Å] complete the trans-C_2NO_4 donor set; the C13—Sn—C20 angle = 171.93(7)°. The different modes of coordination exhibited by the carboxylate ligand are reflected in the associated C—O bond lengths, being equivalent for the O1-carboxylate ligand [C1—O1 = 1.263(2) Å & C1—O2 = 1.259(2) Å] and disparate for the monodentate O3-carboxylate residue with the shorter bond associated with the formal C7=O4 bond [C7—O3 = 1.277(2) Å & C7—O4 = 1.245(2) Å]. An intramolecular water-O—H···O(carboxylate) hydrogen bond is noted [O1w—H1w···O4: H1w···O4 = 1.722(14) Å, O1w···O4 = 2.5557(18) Å with angle at H1w = 169(2)°], i.e. involving the non-coordinating O4 atom.

The most prominent feature of the molecular packing of (I) is the formation of linear, supramolecular chains mediated by water-O—H···N(pyridyl) hydrogen bonds [O1w—H2w···N1^{i}: H2w···N1^{i} = 1.870(19) Å, O1w···N1^{i} = 2.707(2) Å with angle at H2w = 173(2)° for symmetry operation (i) $2 - x$, $1 - y$, $-z$] and parallel to [−1 0 1]. The chains pack without directional interactions between them.

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